Comment on the Relevance of Phosphorus and Sulfur 3d Orbitals

Edgar Müller*

Since the times of Valence Bond (VB) theory, which assigned a 2-electron orbital to each chemical bond, textbooks on phosphorus and sulfur [1] often emphasize the importance of the empty 3d orbitals on these elements, in an attempt to rationalize the differences between them and their corresponding first-row homologues. Noteworthy features, displayed by the second-row elements, include:

1) Hypervalence (i.e., the easy formation of PR₅, PR₆, SR₅, and SR₆ compounds while the agreed ‘maximal valence’, according to the octet rule, would be four),

2) Softness of P- and S-ligands, compared to their N- and O-homologues: π-acidity, back-bonding, stabilization of carbanions at phosphorus or sulfur atoms (Wittig reagents).

In the framework of the VB formalism [2], both features are ‘explained’ with the help of spd-hybrid orbitals. Specifically, sp³d hybrids are invoked for trigonal bipyramidal geometries at P, and sp³d² hybrids for octahedral geometries at S [3]. The VB theory, which offered a theoretical justification for the organic chemist’s intuitive and experimentally founded concept of valence [4], fails, however, short in explaining chemical bonding in a more general context. Phenomena like electron-deficient cluster bonds or solid-state metallic bonds are definitely out of its range; they require a molecular orbital (MO) treatment. Even the organic chemist’s familiar concepts of sp, sp², and sp³-hybridized C-atoms cannot be maintained in the light of quantum physics: it is in fact possible to make four equal chemical bonds out of three p orbitals alone; the s orbital is not really needed! The only requirement is, that the symmetry of the coordination geometry (tetrahedral in this case) coincides with the symmetry of the electron cloud, as a corollary of the Jahn-Teller theorem. The experimental fact that ESCA spectroscopy yields two valence-shell ionization peaks at two different energies for sp³ methane (corresponding to the carbon p and s-shell ionizations, respectively) [5], can be viewed as a decisive disproof of the VB formalism, which, in turn, would predict only one such peak in this case. The localized sp³-hybrid orbitals, although obtained by a unitarian transformation from the atomic (s,p) basis orbital set, are no longer stationary solutions of the molecular Schrödinger equation; to all evidence, these hybrid orbitals are coupled together by the electron-electron repulsion operator, and a rediagonalization splits them up again into s and p waves!

The substitution of the chemically founded, ambiguous concept of valence by the better defined concepts of oxidation state (‘main valence’) and coordination number (‘secondary valence’) was first effected by A. Werner in his ‘Neue Anschauungen auf dem Gebiete der Anorganischen Chemie’ [6], and has opened the way for a rapid rationalization of all aspects of inorganic chemistry after the advent of quantum mechanics. In the field of organic chemistry, however, the conventional valence concept kept much longer alive, as it apparently did a good job in almost all of the known cases [7].

The VB formalism in organic chemistry got furthermore an unexpected boost by the popularization of R. Hoffmann’s extended Hückel method [8], where additional d functions in the basis orbital sets of the elements Si, P, S, and Cl turned out to improve the results substantially [9]. Had not MO theory finally joined the chemist’s intuitive view, that elements which show more than four conventional valences must also have more than four available 2-electron orbitals?

The answer to this question is given by a series of Herman-Skillman atomic struc-

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Table 1. Conventional ICON Parameterization for Si, P, S, and Cl [14]

<table>
<thead>
<tr>
<th>Element</th>
<th>gχ</th>
<th>gδ</th>
<th>Es [eV]</th>
<th>Ep [eV]</th>
<th>Ed [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.383</td>
<td>1.383</td>
<td>-17.3</td>
<td>-9.2</td>
<td>-6.0</td>
</tr>
<tr>
<td>P</td>
<td>1.600</td>
<td>1.400</td>
<td>-18.6</td>
<td>-14.0</td>
<td>-7.0</td>
</tr>
<tr>
<td>S</td>
<td>1.817</td>
<td>1.500</td>
<td>-20.0</td>
<td>-13.3</td>
<td>-8.0</td>
</tr>
<tr>
<td>Cl</td>
<td>2.033</td>
<td>2.033</td>
<td>-30.0</td>
<td>-15.0</td>
<td>-9.0</td>
</tr>
</tbody>
</table>
The results of these calculations show that the 3d orbitals are throughout energetically high-lying \((E = -1.5 \, \text{eV})\) and diffuse (Slater-zeta = 0.35) orbitals for the elements Si to Ar. Their contribution to bonding is thus small [12]. It is noteworthy that the energies of the 4s and 4p orbitals lie throughout below the energies of the 3d shell \((-2.9 \text{ to } -3.7 \, \text{eV})\) and \(-2.0 \text{ to } -2.5 \, \text{eV},\) respectively) and that the 4s and 4p orbitals are much less diffuse (Slater-zetas = 0.61-0.75 and 0.47-0.58, respectively) than the 3d orbitals. If higher-lying atomic orbitals were to play a role in the chemistry of Si, P, S, and Cl, one had thus first to look about the 4s and 4p orbitals!

Potassium is the very first element, where the 3d orbitals may play a chemical role. In the K\(^+\) ion, the 3d orbitals lie merely 2.3 eV above the 4s orbital and have very similar Slater-zeta values. For calcium, the empty 3d orbitals fall already below the 4s orbital. The fact that calcium still shows an (Ar)s\(^2\)-ground-state configuration is due to the higher interelectronic repulsion exerted by the atomic field on an electron in a 3d orbital, compared with that exerted on an electron in a 4s orbital. The (Ar)s\(^2\) state has thus a higher overall energy than the (Ar)s\(^2\) state. The 3d orbitals play also a role in the Ca\(^{2+}\) ion, where they lie below the 4s orbitals by 2.2 eV. The marked particularities in catalytic behavior of potassium and calcium compounds, compared to their earlier homologues of sodium and magnesium, may thus well be explained on such grounds. The elements following calcium, i.e., scandium and titanium, have already an occupied 3d shell in their atomic ground state.

The chemical irrelevance of the 3d orbitals for elements with atomic numbers lower than or equal to 18 (Ar) is also emphasized by the results of scattering theory. S.T. Manson [13] of the American National Bureau of Standards calculated the electron scattering phase shifts as a function of electron energy and atomic number. He found that no appreciable phase shift is exerted on electronic d waves of low energy by the field of atoms with ordinal numbers lower or equal 18. This means that bonding interaction with 3d orbitals is energetically irrelevant for the elements preceding potassium! In a similar way, Manson shows that 4f orbitals
KOLUMNE
start to play a chemical role at earliest at
atom number 55 (Cs) or 56 (Ba).
The '3d orbitals' used by R. Hoffmann
et al. in their extended-Hückel calcula-
tions on Si, P, S, and Cl compounds can,
therefore, by no means be real 3d orbitals.
This is shown as well by the recommended
parameter set for the ICON program (Ta-
ble 1) [14], which deviates very much from
what is obtained from atomic structure
calculations (Table 2). The 'd orbitals'
in Table 1 merely play a role as polariza-
tion functions, enlarging the basis sets of
the variational calculi and enabling the
resulting wave-functions to get closer to
the real molecular wave-functions. In this
context, one could use, with equal success,
double- or triple-zeta expansions for the
second-row elements' s and p orbitals,
because every additional component in
the basis set of any imaginable type, will
enhance the accuracy of the variational-
ly obtained molecular wave-functions. In a
later paper, R. Hoffmann and coworkers
explicitly discuss about the deus ex machi-
na role that d functions were to play during
some time in second-row elements' chem-
istry, concluding that such functions were
at best useful as a calculation trick to
enhance the precision of the EH energies
[15].

But how to reply then to the more
difficult arguments of hypervalence and
softness of the second-row elements Si, P,
S, and Cl?

1) Hypervalence is a concept formulated
with respect to the VB formalism. It poses
by no means a problem in the
framework of quantum theory, in which
the chemical bonding does not depend
on the availability of a 2-electron orbital
for every chemical bond of a mole-
cule. The pseudoproblem of hypervalen-
cence can most easily be solved through
a rigorous substitution of the some-
what ambiguous concept of 'valence'
by the better defined concepts of 'oxi-
dation state' and 'coordination num-
ber', along A. Werner's guidelines. The
quantum-chemical requirement for a
stable bonding situation is merely, that
coordination geometry and electron con-
figuration of a molecule are sym-
metry compatible.

2) Softness can be explained by the lower
bond strengths of the bonds involving
second-row elements, compared to
bonds involving first-row elements. A
low bond strength means, however, that
the molecule has low-lying anti-
bonding orbitals, or, in other words,
remaining unsaturated valence! The
bonds may easier be formed and bro-
ken in such a situation, and the atom
may also be involved into more bonds
at a time. π-Acidity and backbonding in
phosphines and thio-compounds are,
therefore, rather tied to the presence of
low-lying antibonding (σ*) orbitals than
to the presence of empty 3d orbitals.
The observation of, e.g. a length-
ening of the P–C bonds in alkyl-
ary phosphine complexes, in which the
P-atom acts as a π-acid, could be a
proof of this statement [16]. Such a
lengthening would, in contrast, not
occur in the case where the acceptor
orbitals were phosphorus 3d orbitals.

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of Fribourg, is cordially acknowledged for a copy of
the Herman-Skillman Program as well as for advice
concerning the exchange functional.

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[1] See, e.g. J.B. Hendrickson, D.J. Cram, G.S.
Hammond, 'Organic Chemistry', 3rd edn.,
'Sulphur and Phosphorus'; H. Kwart, K.
King, 'd-Orbitals in the Chemistry of Sili-
con, Phosphorus and Sulfer', Series 'Reac-
tivity and Structure Concepts in Organic
Chemistry', Springer-Verlag, Berlin, 1977,
Vol. 3.

Oxford University Press, Oxford, 1994,
Chapt. 14.

Bond', Cornell University Press, Ithaka,
1938.

[4] Remember that atomism was a working
postulate of chemistry long before experi-
mental proofs for the real existence of
atoms were available: John Dalton, 'A New
System of Chemical Philosophy', 1808;
and that the concepts of chemical valence
and chemical bond were formed long before
any physical explanation of the nature of
these phenomena could be given. E. Frank-
MO theory as well as the application of
other exact physical methods to chemistry
must have been perceived (and are, maybe,
still perceived) by certain chemists as an
intrusion of physics into someone else's
preserves.

Bundle, 'Molecular Photoelectron Spectro-
scopy; A Handbook of He 584 Å Spectra',

Gebiete der Anorganischen Chemie',
Friedr. Vieweg & Sohn, Braunschweig,
editions 1905, 1908, 1913, 1919. See also
the contributions in Helv. Chim. Acta 1967,
'Fasciculus Extraordinarius Alfred Werner'.

[7] The need for revisions became only appar-
ent at very recent times, when metallo-
organic chemistry revealed the existence
of such things as sandwich compounds,
penta- and hexacoordinated carbon atoms
in metal clusters and agnostic interactions
of protons, carbonations, and metal centers
with saturated C–H and C–C bonds.

1397.

[9] R. Hoffmann, J. M. Howell, E.L. Muetter-

Calculations', Prentice-Hall, Inc., Engle-
version of the original program was used,
which includes J.P. Perdew's empirical
parameter free GGA91 exchange func-
tional, combined with R. Latter's full cor-
rection of the exchange potential. For the
underlying theory see: J. P. Perdew, Wang
Yue, Phys. Rev. B 1986, 33, 8800; and R.
Latter, Phys. Rev. 1955, 99, 510. Slater-
type orbitals were fitted to the outer parts
of the obtained numerical wave-functions,
and the corresponding zeta values (ζ) are
reported together with the energies (E) of
the orbitals.

[11] The disturbance of an atom due to its
chemical environment is relatively small com-
pared with the binding energies of the elec-
trons in the atom itself; even in the case of
the most affected valence electrons, the
calculated effects amounts to only 10–20% of
the electron's total binding energy.

[12] The stabilizing effect of an empty orbital
onto energetically lower-lying electrons
becomes negligible, when the energy level
of the empty orbital approaches the vacuum
level (zero).


R. Hoffmann, ICONS, Quantum Chemis-
try Program Performing Extended Hückel
Calculation; Quantum Chemical Program
